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(71)Applicant : SUMITOMO BAKELITE CO LTD

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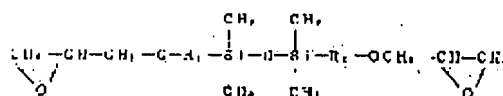
(72)Inventor : KOBAYASHI MICHIO

(54) ANISOTROPICALLY CONDUCTIVE FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the storage stability at ordinary temperature, the adhesiveness in a wide temperature range, the stability of connection resistance, etc., and minimize the residual strain at a joint by using a specified polyvinyl butyral resin and three other specified components as the essential constituents.

SOLUTION: This film essentially comprises a polyvinyl butyral resin (A) having a degree of polymerization of 1,500 to 2,500, a degree of acetylation of at most 3mol%, a degree of butyralization of at least 65mol% and a flow softening point of at least 200°C, an epoxy resin (B) having at least two epoxy groups in the molecule, a reaction product (C) of an imidazole derivative having active hydrogen atoms in the molecule with a silicone epoxy compound of the formula (wherein R1 and R2 are each a divalent 1-5C aliphatic group, or a residue of a 6C or higher aromatic group having two hydrogen atoms removed therefrom) at a molar ratio of (1.5 to 2.5):1, and conductive particles (D) having a particle diameter of 3-15μm, with a mean particle diameter of 5-10μm, and comprising a high-molecular spherical core material having a metal coating on the surface. The components A to D are dissolved or dispersed in a solvent,



and the solution or dispersion is cast on a polyester film treated to render releasable, which is then heat treated.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrical installation of detailed circuits, and the different direction electric conduction film used for connection between LCD (liquid crystal display), and the flexible circuit board and a TAB film, and micro junction of a semiconductor IC and IC loading circuit board in more detail.

[0002]

[Description of the Prior Art] With the miniaturization of the latest electronic equipment, and thin-shape-izing, needs, such as connection of detailed circuits and connection of minute components and a detailed circuit, are increasing by leaps and bounds, and the electroconductive glue and the film of an anisotropy are beginning to be used as the connection method. (For example, JP,59-120436,A, 60-191228, 61-274394, 61-287974, 62-244242, 63-153534, 63-305591, 64-81878, Taira 1-46549, 1-25178 each number official report, etc.) . In connection of the circuits by the anisotropy electric conduction film accompanying [detailed-ization of the further component progresses and] it The demand to it being possible to exfoliate and to carry out recompression arrival of the wired member connected once for the reasons of a location gap etc., without being damaged or damaged, (the so-called "repair"), Based on the distortion stress of the resin in the inside of hardening contraction and the various ambient atmospheres of the heat-curing reaction time of a different direction electric conduction film itself, the problem that adherend is damaged (for example, the crack of the glass substrate used for LCD and curvature of a substrate) is arising. In order to solve these problems, the different direction electric conduction film of further low distortion fast hardening, long LIFE, moisture resistance, and high-reliability heat-curing type is demanded strongly.

[0003]

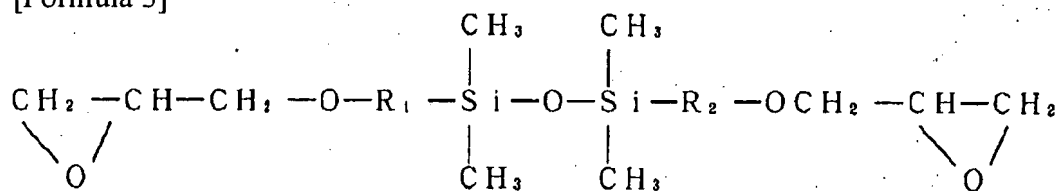
[Problem(s) to be Solved by the Invention] This invention has the adhesive property which was not acquired in the conventional heat-curing mold and which was excellent, carried out heating pressurization and was excellent in the storage stability in ordinary temperature after hardening in the wide range temperature field (-40 degrees C - 100 degrees C), and its distortion (stress) which moreover remains in a joint is very small, and it offers the heat-curing type different direction electric-conduction film with which after severe processing still like moisture resistance was excellent in the stability of connection resistance.

[0004]

[Means for Solving the Problem] This invention is a different direction electric conduction film with which a degree of polymerization uses as an indispensable component the electric conduction particle (D) to which whenever [less than / 3 mol % / and butyral-ized] has [whenever / 1500-2500, and acetylation / more than 65 mol % and flow softening temperature] metallic coating on a reactant (C) with the silicone epoxy compound expressed with the polyvinyl butyral resin (A) which has the property of 200 degrees C or more, an epoxy resin (B), an imidazole derivative, and a formula (1), and the front face of macromolecule spherical karyomitome.

[0005]

[Formula 3]



(1)

(R1 and R2 show the residue excluding two hydrogen from with the aliphatic series radical of the divalent carbon numbers 1-5, or a carbon numbers of six or more aromatic series, and even if mutually the same, they may differ)

[0006]

[The mode of implementation of invention] Although the polymerization degree of the polyvinyl butyral resin used for this invention is 1500-2500, if polymerization degree is less than 1500, the resin fluidity at the time of heating and pressurization will become it is large and inadequate [adhesive strength]. Moreover, if polymerization degree exceeds 2500, the fluidity of resin runs short, an electric conduction particle cannot contact a terminal, and conductivity is not obtained. Moreover, although whenever [polyvinyl butyral resin's used for this invention acetylation] is less than [3 mol %], if whenever [butyral-ized] is less than [65 mol %], the polyvinyl alcohol in a molecule and the content rate of polyvinyl acetate increase, and adhesive strength is insufficient [if three mol % is exceeded, affinity with adherend (a LCD glass substrate and TAB film) worsens and adhesive strength is insufficient, and]. Furthermore, although the flow softening temperature of polyvinyl butyral resin is 200 degrees C or more, if it is less than 200 degrees C, winning of air bubbles becomes [the resin fluidity at the time of heating and pressurization] large greatly, and adhesive strength is insufficient for it.

[0007] The epoxy resin used for this invention has at least two or more epoxy groups in 1 molecule.

Specifically The bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, As an epoxy resin which has a naphthalene frame in a molecule besides being a bisphenol smooth S form epoxy resin, a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, etc. 1, 6-screw-(2, 3-epoxy propoxy) naphthalene or 2, the resin that reacted the condensate of 7-dihydroxy naphthalene and formaldehyde with EPIKUDORUHI drine compounds, Although EPIKUDORUHI drine compounds, the resin which reacted are mentioned in the condensate of 2-hydroxy naphthalene, 2 and 7-dihydroxy naphthalene, and formaldehyde, it is not limited to these things, and even when it is independent, even if it mixes and uses, it does not interfere.

[0008] As an imidazole derivative used for this invention, what has active hydrogen is mentioned to intramoleculars, such as 2-methylimidazole, 2-ethyl imidazole, 2-undecylimidazole, a 2-hepta-JISHIRU imidazole, 2-phenylimidazole, 2-ethyl-4-methylimidazole, 2-phenyl-4-methylimidazole, 2-phenyl-4-methyl-5-hydroxymethylimidazole, and 2-phenyl-4, 5-dihydroxymethylimidazole, for example. Although the silicone epoxy compound used for this invention is shown by the formula (1), its thing of the structure shown by the formula (2) which is a propylene radical as R1 and R2 is desirable from the ease of industrial acquisition. The reactant of the imidazole derivative and silicone epoxy compound which are used for this invention mixes an imidazole derivative and a silicone epoxy compound at a rate of the brewing mole ratios 1.5-2.5, adds a solvent as occasion demands, on conditions 100 degrees C or more, is made to react for 1 to 100 hours, and is obtained. If a brewing mole ratio exceeds 2.5, in order that an imidazole derivative may remain as an unreacted component, when this is used, the shelf life of a resin constituent falls. Moreover, since a silicone epoxy compound will remain as an unreacted component and hardenability will fall if it is less than 1.5, it is not desirable. By the class and brewing mole ratio of an imidazole derivative, this reactant is in a condition solid with ordinary temperature, or liquefied, and is used as a curing agent of an epoxy resin. In order to improve shelf life further, in a solid case, pulverization of this reactant is carried out, it is made to react with a little isocyanate compound,

performs surface treatment, and although you may use independently, when liquefied, it may microencapsulate and use it with polyurethane resin etc. A reactant is 5 - 200 weight ***** to the epoxy resin 100 weight section. If there is little effectiveness in hardenability, moisture resistance, and stress nature in case of under 5 weight sections and the 200 weight sections are exceeded, shelf life and bond strength will fall. An imidazole derivative, amines, a phenols acid anhydride, etc. may be used together that what is necessary is just the curing agent for epoxy resins used from the former as curing agents other than a reactant.

[0009] In this invention, there are few falls of the adhesive strength at the time of low temperature and an elevated temperature in order to use the epoxy compound containing the low chain length siloxane unit shown by the formula (1), and since hygroscopicity also has few still more moderate flexibility and stress also decreases, a different direction electric conduction film with little degradation after moisture absorption processing and thermo-cycle processing is obtained.

[0010] Although the electric conduction particle which has metallic coating on the front face of the macromolecule spherical karyomitome used by this invention has the nickel film on the front face of macromolecule spherical karyomitome and is an electric conduction particle of this nickel film which has a gold film in an outer layer further Although especially the thickness of the coat of the gold film of an electric conduction particle front face and the nickel film is not limited, since conductivity will become unstable, and too thick grain child deformation will become difficult or condensation etc. will arise if too thin, the thickness of gold and a nickel coat has desirable 0.01-1 micrometer. Moreover, it is good to be formed in homogeneity by the formation approach of a coat in consideration of the adhesion force with the macromolecule spherical karyomitome used as this coat and core, conductivity, etc., and the electroless deposition used from the former is desirable.

[0011] Moreover, it is desirable that the particle size of the electric conduction particle which has metallic coating on the front face of the macromolecule spherical karyomitome used for this invention is 3-15 micrometers, and mean particle diameter is 5-10 micrometers. Particle size cannot absorb near in the magnitude of the irregularity on the front face of a circuit which they will connect if less than 3 micrometers and mean particle diameter are less than 5 micrometers, and cannot absorb variation in circuit thickness at the time of thermocompression bonding, but causes an increase of connection resistance, and poor opening. Moreover, when particle size exceeds 15 micrometers, and 10 micrometers of mean diameters were exceeded and a circuit pitch (circuit width-of-face + circuit spacing) applies to 0.1mm or less, a particle contacts between adjoining circuits, the insulation between adjoining circuits falls or there is a danger of causing short-circuit. What is necessary is just to choose an optimum value by a circuit terminal pitch, terminal thickness variation, etc. which are connected within the limits of these. For example, the particle size of the electric conduction particle which has metallic coating in connection with the liquid crystal display panel and the flexible circuit board (henceforth, FPC) which are the main applications of a different direction electric conduction film is about 3-15 micrometers, and the loadings to insulating adhesives have desirable 0.5 - 10 volume %. Moreover, the compression disruptive strength of the electric conduction particle which has metallic coating on the front face of macromolecule spherical karyomitome is 2, and 10-100kg/mm of 100-1000kg /of compressibility is [mm] 2. Before compression disruptive strength obtains electrical installation as less than [10kg //mm] 2 and compressibility are less than [100kg //mm] two, a particle will be destroyed and it cannot connect. Moreover, when compression disruptive strength exceeds 2 [100kg / /] mm and compressibility exceeds 2 [1000kg / /] mm, it becomes the cause on which an excessive pressure must be put for obtaining sufficient area for connection of a terminal and a terminal and which damages adherend. In order to crush the metallic-coating particle after thermocompression bonding and for condition to affect many properties, such as connection dependability, compression disruptive strength needs to be 2 and 10-100kg/mm of 100-1000kg /of compressibility needs to be [mm] 2.

[0012] Although especially the presentation of macromolecule spherical karyomitome is not limited, polymers, such as an epoxy resin, urethane resin, melamine resin, phenol resin, acrylic resin, polyester resin, styrene resin, and a styrene-butadiene copolymer, are mentioned, for example, and even when these are independent, even if it mixes and uses them, they do not interfere. Moreover, Au, nickel, Ag,

Cu, Zn, Sn, In, aluminum, Pd, etc. are mentioned to metallic coating, and these may combine with it. These macromolecule spherical karyomitome and metallic coating should just choose a suitable thing in consideration of both adhesion force etc.

[0013] The different direction electric conduction film of this invention is obtained by casting into thickness uniform on a polyester system film or a fluorine system film etc. which carried out mold release processing, and vaporizing a solvent in heat treatment, after choosing (A) - (D) component suitably, using a solvent and dissolving or distributing homogeneity. Improvement in workability or various engine performance is aimed at, and even if it adds suitably various additives, for example, a nonresponsive diluent, a reactant diluent, a thioxotropy grant agent, a coupling agent, a thickener, an inorganic filler, etc., it does not interfere.

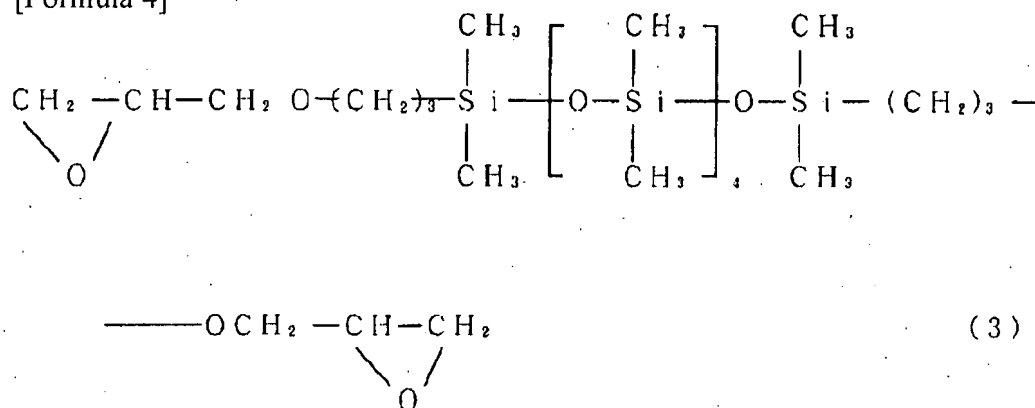
[0013] Warming and agitating example of manufacture 12-undecyl imidazole (molecular weight 222) 44.4g (0.2 mols) of a reactant at 150 degrees C, added gradually 39.2g (molecular weight 392) (0.1 mols) of silicone epoxy compounds of the aforementioned formula (2), and carried out the temperature up to 170 degrees C, it was made to react for 3 hours, and the brown and viscous product was obtained. This product is used as a resultant (1).

Warming and agitating example of manufacture 22-heptadecyl imidazole (molecular weight 306) 61.2g (0.2 mols) of a reactant at 150 degrees C, added gradually 39.2g (0.1 mols) of silicone epoxy compounds of the aforementioned formula (2), and carried out the temperature up to 180 degrees C, it was made to react for 5 hours, and the brown and viscous product was obtained. This product is used as a resultant (2).

[0014] Warming and agitating example of manufacture 32-undecyl imidazole 44.4g (0.2 mols) of a reactant at 150 degrees C, added gradually 66g (molecular weight 660) (0.1 mols) of epoxy compounds containing the long-chain siloxane unit expressed with a formula (3), carried out the temperature up to 180 degrees C, it was made to react for 10 hours, and the brown and viscous product was obtained. This product is used as a resultant (3).

[0015]

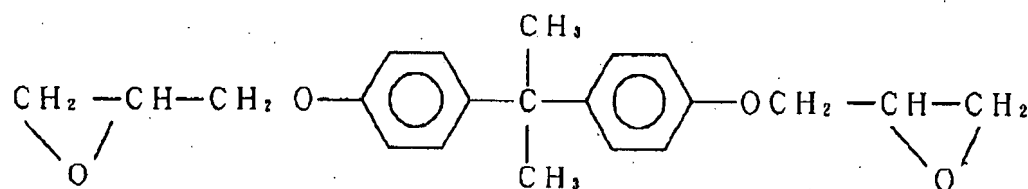
[Formula 4]



[0016] Warming and agitating example of manufacture 42-undecyl imidazole 44.4g (0.2 mols) of a reactant at 120 degrees C, added gradually 34.0g (molecular weight 340) (0.1 mols) of epoxy compounds which do not contain the siloxane unit expressed with a formula (4), it was made to react at 120 more degrees C for 5 hours, and the product solid in red was obtained. What pulverized this product to about 20 meshes is used as a resultant (4).

[0017]

[Formula 5]



(4)

[0018] The example of manufacture 52-undecyl imidazole of a reactant was reacted like the example 1 of manufacture except using 66.6g (0.3 mols), and the resultant (5) was acquired.

The example of manufacture 62-undecyl imidazole of a reactant was reacted like the example 1 of manufacture except using 22.2g (0.1 mols), and the resultant (6) was acquired.

[0019] An example explains this invention concretely below.

As an example 1 reactivity elastomer, whenever [degree-of-polymerization 1700 and acetylation] Less than [3 mol %], The solution which dissolved the polyvinyl-butyril-resin 25 weight section more than 65 mol % and whose flow softening temperature are 225 degrees C whenever [butyril-ized] so that it might become 10 % of the weight at toluene / ethyl-acetate =5:1 (weight ratio) mixed solution, The solution which dissolved the amount bisphenol A mold epoxy resin of giant molecules (weight per epoxy equivalent 4000) 25 weight section in toluene / butyl-acetate =3:1 mixed solution so that it might become 50 % of the weight, The low-molecular-weight bisphenol A mold epoxy resin (weight per epoxy equivalent 200) 40 weight section, Carry out 4 weight sections addition of the electric conduction particle (mean particle diameter of 5 micrometers) which carried out churning mixing of the resultant (1) 40 weight section promptly, and carried out nickel/Au plating at this at polystyrene spherical karyomitome, and it distributes to homogeneity. Furthermore, toluene was added, on the 4-fluoride ethylene-perfluoroalkyl vinyl ether copolymer film, it cast and dried and the different direction electric conduction film whose thickness is 25 micrometers was obtained. The result of having carried out evaluation after various processings of shelf life, adhesive strength, and connection resistance about this different direction electric conduction film is shown in Table 1. Shelf life was made into O, when connection resistance when a film is connected at a room temperature (23 degrees C) and it connects ITO glass with TAB after neglect for seven days at 40 degrees C for 30 days was rising 20% or more to early connection resistance and it was the rise below $x < 20\%$. TAB (pitch 0.10mm --) by which adhesive strength performed 0.4-micrometer tinning to copper foil / polyimide =35 / 75 micrometers as adherend 200 terminal numbers and ITO glass with a thickness [in which with a sheet resistance / of 30 ohms / the indium / stannic acid ghost electric conduction coat were formed on the whole surface] of 1.1mm are used. For both the different direction electric conduction film of 2mm width of face by the pressure of 30kg/cm² 90-degree friction test estimated the sample stuck by pressure for 30 seconds at 180 degrees C. Connection resistance computed the average by having measured the connection resistance between the terminals of 200 terminals using the above-mentioned sample.

[0020] According to combination of two to example 6 table 1, the different direction electric conduction film was adjusted by the same approach as an example 1, and the same trial as an example 1 was performed. An evaluation result is shown in Table 1.

As the example 1 of a comparison, and a 2 reactivity elastomer, in the example 1 of a comparison, whenever [degree-of-polymerization 300 and acetylation] exceeded three-mol %, and the different direction electric conduction film was obtained like the example 1 whenever [butyril-ized] except having used [whenever / degree-of-polymerization 1000 and acetylation] polyvinyl butyril resin of 160 degrees C of 70-mol % and flow softening temperatures for polyvinyl butyril resin of 115 degrees C of 63 **three-mol % and flow softening temperatures whenever [less than / 3 mol % / and butyril-ized] in the example 2 of a comparison. An evaluation result is shown in Table 2.

Three to example of comparison 6 resultant (3) The different direction electric conduction film was prepared by the same approach as an example 1 except using - (6). An evaluation result is shown in

Table 2.

[0021]

[Table 1]

表1

			実施例					
			1	2	3	4	5	6
ポリビニルブチラール樹脂(重合度1700)			25	25	25	25	25	25
高分子量ビスフェノールA型エポキシ樹脂			25	25	25	25	25	25
低分子量ビスフェノールA型エポキシ樹脂			40	50	20		40	
1, 6-ビス(2, 3-エポキシプロポキシ)ナフタレン					20	40		40
反応生成物(1)			40	50	40	40		
反応生成物(2)							40	40
導電粒子			4	4	4	4	4	4
保存性	室温		○	○	○	○	○	○
	40℃		○	○	○	○	○	○
接着力 (g/cm)	初期	室温	850	810	850	920	780	810
		60℃	820	800	810	880	790	770
	500時間後 *1	室温	790	800	780	850	750	740
		60℃	810	770	760	820	740	760
接続抵抗値	室温		1.8	1.6	1.7	1.6	2.0	1.9
	500時間後 *1		2.4	2.0	2.2	1.9	2.7	2.5
	温湿度サイクル500サイクル後 *2		2.6	2.3	2.4	2.2	2.9	2.5

*1: 85℃、85%相対湿度の恒温恒湿槽

*2: (-40℃/30分)、(25℃/5分)、(85℃、85%相対湿度/30分)を1サイクルとして、500回繰り返す

[0022]

[Table 2]

表2

			比較例					
			1	2	3	4	5	6
ポリビニルブチラール樹脂(重合度1700)					25	25	25	25
ポリビニルブチラール樹脂(重合度300)			25					
ポリビニルブチラール樹脂(重合度1000)				25				
高分子量ビスフェノールA型エポキシ樹脂			25	25	25	25	25	25
低分子量ビスフェノールA型エポキシ樹脂			40	40	40	40	40	40
反応生成物(1)			40	40				
反応生成物(3)					40			
反応生成物(4)						40		
反応生成物(5)							40	
反応生成物(6)								40
導電粒子			4	4	4	4	4	4
保存性	室温		○	○	○	○	×	○
	40℃		○	○	○	○	×	○
接着力 (g/cm)	初期	室温	590	810	650	850	800	610
		60℃	450	740	420	830	730	400
	500時間後 *1	室温	500	730	530	740	740	470
		60℃	310	700	270	690	700	290
接続抵抗値	室温		1.9	3.9	2.4	1.9	2.0	4.1
	500時間後 *1		2.8	5.8	4.1	3.5	2.9	7.9
	温湿度サイクル500サイクル後 *2		3.2	7.2	5.8	15.1	3.3	17.5

*1: 85℃、85%相対湿度の恒温恒湿槽

*2: (-40℃/30分)、(25℃/5分)、(85℃、85%相対湿度/30分)を1サイクルとして、500回繰り返す

[0023]

[Effect of the Invention] According to this invention, it is usable to the detailed micro junction below 0.05mm pitch, and excels in adhesive strength, and a reliable different direction electric conduction film can be obtained.

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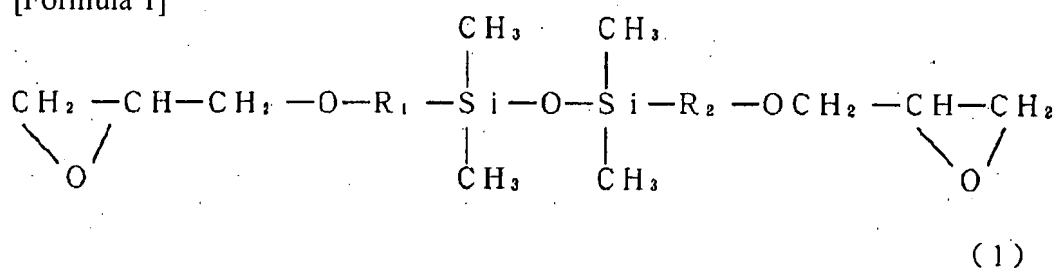
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CLAIMS

[Claim(s)]

[Claim 1] The different direction electric conduction film with which a degree of polymerization is characterized by using as an indispensable component the electric conduction particle to which whenever [less than / 3 mol % / and butyral-ized] has [whenever / 1500-2500, and acetylation / more than 65 mol % and flow softening temperature] metallic coating on a reactant (C) with the silicone epoxy compound expressed with the polyvinyl butyral resin (A) which has the property of 200 degrees C or more, an epoxy resin (B), an imidazole derivative, and a formula (1), and the front face of macromolecule spherical karyomitome.

[Formula 1]

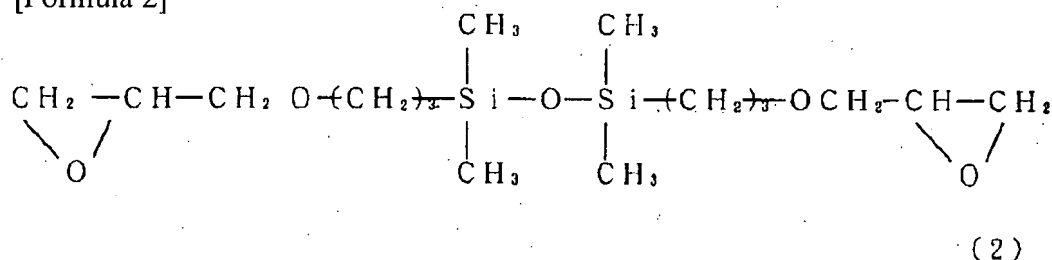


(R1 and R2 show the residue excluding two hydrogen from with the aliphatic series radical of the divalent carbon numbers 1-5, or a carbon numbers of six or more aromatic series, and even if mutually the same, they may differ)

[Claim 2] The different direction electric conduction film according to claim 1 whose reaction mole ratios of a silicone epoxy compound expressed with an imidazole derivative and a formula (1) are 1.5-2.5.

[Claim 3] The different direction electric conduction film according to claim 1 or 2 whose silicone epoxy compound expressed with a formula (1) is the following formula (2).

[Formula 2]



[Claim 4] Claim 1 whose mean particle diameter the particle size of the electric conduction particle which has metallic coating on the front face of macromolecule spherical karyomitome is 3-15 micrometers, and is 5-10 micrometers, a different direction electric conduction film according to claim 2 or 3.

[Translation done.]